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## PATENT ABSTRACTS OF JAPAN

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## (54) IMAGE FORMING METHOD BY POWDER TONER

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonmagnetic one component development method which is excellent in image quality and reduces toner consumption per page.

SOLUTION: A developer is supplied to a photoreceptor and the electrostatic latent image on this photoreceptor is developed to a sensible image by using a nonmagnetic one component development device having at least a developer carrying roll and a layer forming member. In such a case, spherical toners having a volume average grain size of 2 to 6  $\mu\text{m}$  are used as the developer. The toner adhesion on the developer carrying roll is specified to a range from  $\geq 0.1 \text{ mg/cm}^2$  to  $\leq 0.45 \text{ mg/cm}^2$ .

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**CLAIMS**


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[Claim(s)]

[Claim 1] A nonmagnetic 1 component development method characterized by toner coating weight on a developer support roll being the range of two or more to two or less 0.45 mg/cm using a globular form toner whose volume mean particle diameter is 2-6 micrometers as a developer in a nonmagnetic 1 component development method which supplies a developer to a photo conductor and actualizes an electrostatic latent image on a photo conductor using a nonmagnetic 1 component developer which has a developer support roll and a stratification member at least [ 0.1 ]

[Claim 2] A nonmagnetic 1 component development method according to claim 1 using a globular form toner whose content of this carbon black a coloring agent is 8 % of the weight or more in carbon black as a developer at styrene (meta) acrylic resin for resin for binding.

[Claim 3] A nonmagnetic 1 component development method according to claim 1 using a globular form toner whose content of this organic pigment a coloring agent is 3 % of the weight or more in an organic pigment as a developer at polyester resin for resin for binding.

[Claim 4] An according to claim 1, 2, or 3 nonmagnetic-in average circularity (perimeter of circle of same area as particle projected area) (average of circularity defined by / (perimeter of particle projection image)) by which endocyst of coloring agent was carried out to resin for binding as developer 1 component development method using 0.97 or more globular form toners.

[Claim 5] An image formation method according to claim 1, 2, 3, or 4 that 50% volume particle size / 50% number particle size is [ particle size distribution of a globular form toner used as a developer ] 1.25 or less, and a square root of 84% volume particle size / 16% volume particle size is 1.25 or less.

[Claim 6] A nonmagnetic 1 component development method according to claim 1, 2, 3, 4, or 5 that only an amount an inorganic oxide particle is indicated to be by degree type is \*(ed) outside by globular form toner particle used as a developer.

[A formula 1]

$3.5714X - 0.9942 \leq Y \leq 31.399X - 0.9477$  -- [ -- outside \*\*\*\* [ as opposed to / Y / here / as opposed to / in X / volume mean particle diameter (micrometer) of a toner particle / \*\*\*\* / a toner particle ] (% of the weight). ]

[Claim 7] A nonmagnetic 1 component development method according to claim 4, 5, or 6 acquired by method of taking out this particle that a toner particle makes mix and emulsify an organic solvent solution which uses a coloring agent and resin for binding of nonaqueous solubility as an indispensable component, and aqueous data medium, and is distributing in [ after forming a globular form coloring particle ] liquid data medium as desiccation fine particles.

[Claim 8] A nonmagnetic 1 component development method according to claim 4, 5, or 6 acquired by method of taking out this particle that a toner particle makes carry out the polymerization of the polymerization nature monomer which distributed a coloring agent in liquid data medium, and is distributing in [ after forming a globular form coloring particle ] liquid data medium as desiccation fine particles.

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the suitable new nonmagnetic 1 component development method which can form a quality image to use it for the electrostatic-charge image development in a printer, a copying machine, etc. of an electrophotography method.

[0002]

[Description of the Prior Art] compared with lithography, a film photo, etc., it is markedly alike, the copying machine of the present electrophotography method and the image quality of a printer are inferior, and various amelioration is made from both sides of image formation equipment and the fine-particles toner used for it.

[0003] From the field of a toner, as a means which raises image quality, such as resolution, diameter-ization of a granule becomes important recent years increasingly, and ED is performed variously.

[0004] however, most fine-particles toners for electrostatic-charge image development by which current marketing is carried out — the volume mean particle diameter of about 8-13 micrometers — it is — most — small — and it is about 7 micrometers (measurement of particle size is based on a coal tar multi-sizer (department device of a day)). Thus, the actual condition is that development of the developer which it has now stopped at high resolution-ization of image quality about diameter[ of a granule ]-izing of a very useful toner at about 7 micrometers, and commercial production of the diameter toner of a granule is not performed rather than it, and uses such a toner is also seldom made.

[0005] Then, it waits for the further diameter[ of a granule ]-izing of a toner, grant of the outstanding frictional electrification nature, and development and an appearance of the development method.

[0006] As the process, a fine-particles toner has the grinding method as a dry process, and has a polymerization method, the so-called phase inversion emulsifying method indicated by JP,5-66600,A etc. as a wet method. In the industrial production which used the present grinder in the toner by the grinding method, about 7 micrometers is called limit of diameter[ of a granule ]-izing. Although the about 5-micrometer diameter toner of a granule is also producible, of course, there is a problem of aggravation of the frictional electrification nature accompanying becoming a cost rise and diameter[ of a granule ]-izing of a toner or particulate flow kinesis, and it is hard to say that it is practical.

[0007] In wet methods, such as a polymerization method and the emulsifying method, it is said that diameter-ization of a granule of a fine-particles toner is fundamentally easy. However, in the conventional wet method toner, replacement of the grinding method toner with the above usual mean particle diameter (about 7-13 micrometers) is set as main development or a production aim, it is not known in fragments the place to current about the fine-particles toner whose mean particle diameter is a diameter of a granule about 6 micrometers or less, and the practical formula is not understood.

[0008] On the other hand, since a toner with sufficient diameter of a granule was not able to produce stably as described above although various researches corresponding to diameter[ of a granule ]-izing of a toner are made also about image formation equipment for image upgrading, an image formation equipment side was not fully able to develop the image formation method corresponding to the toner of such a diameter of a granule, either. For this reason, now, the image formation method corresponding to the diameter toner of a granule about 6 micrometers or less in mean particle diameter which makes image formation of high resolution possible is not yet established enough.

[0009]

[Problem(s) to be Solved by the Invention] The purpose of this invention offers the image formation method of high quality using the about 2-6-micrometer diameter fine-particles toner of a granule excellent in frictional electrification nature used for the electrostatic-charge image development of the copying machine of an electrophotography method, or a printer, and offers the development method of nonmagnetic 1 component also especially in it. Improvement in the image quality of a copying machine or a printer is realized by this.

[0010]

[Means for Solving the Problem] Artificers found out that improvement in marked image quality could realize toner coating weight on a developer support roll which was about two 0.5 - 0.7 mg/cm conventionally by setting it as 0.1 - 0.45 mg/cm<sup>2</sup> as a result of repeating examination wholeheartedly aiming at improvement in image quality in nonmagnetic 1 component development. Under the present circumstances, it becomes possible easily to make toner coating weight on a developer support roll into the above-mentioned range by using a globular form toner whose

volume mean particle diameter is 2-6 micrometers.

[0011] Furthermore as a developer for black, a coloring agent was carbon black, artificers were using a globular form toner whose content of this carbon black is 8 % of the weight or more, and in addition to resolution and gradation nature of an image, when they found out that image concentration was realizable with the high level and styrene acrylic resin was especially used as resin for binding, they found out demonstrating a marked effect.

[0012] Artificers were using a globular form toner whose coloring agent's is an organic pigment and whose content of this organic pigment is 3 % of the weight or more as a developer for colors, and when polyester resin was used for high image quality being realizable as a header, especially resin for binding, they found out demonstrating an effect according to rank further again.

[0013] Moreover, average circularity (perimeter of a circle of the same area as particle projected area) (average of circularity defined by / (perimeter of a particle projection image)) was 0.97 or more, and by using a fine-particles toner characterized by carrying out the endocyst of the coloring agent to resin for binding, artificers could attain still more easily conditions of toner coating weight on the above-mentioned developer support, and found out that image quality improved. This is a globular form with high sphericity, and is because a toner layer thin to homogeneity can be formed on a developer support roll by moreover using a toner of a diameter of a granule.

[0014] Furthermore, artificers found out that image quality could be raised further by using a globular form toner characterized by for number particle size being 1.25 or less, and a square root of volume particle size having particle size distribution or less of 1.25 84% volume particle size / 16% 50% volume particle size / 50%.

[0015] Artificers found out that image quality could be raised further further again, when an inorganic oxide particle used a globular form toner by which only an amount shown by degree type is \*(ed) outside.

[0016]

[Formula 1]

$3.5714X - 0.9942 \leq Y \leq 31.399X - 0.9477$  — [ — outside \*\*\*\* [ as opposed to / Y / here / as opposed to / in X / volume mean particle diameter (micrometer) of a particle (C) / \*\*\*\* / a particle (C) ] (% of the weight). ]

[0017] This is because electrification nature and a fluidity which are the important fundamental property of a toner are remarkably improvable by using a toner which fulfilled the above-mentioned conditions.

[0018] An organic solvent solution with which artificers use a coloring agent and resin for binding of nonaqueous solubility as an indispensable component further again, aqueous data medium is mixed and emulsified — making — a solvent after forming a globular form coloring particle — a fine-particles toner obtained by method of taking out this particle currently distributed inside of the body as desiccation fine particles — or By using a fine-particles toner obtained by method of taking out this particle that is made to carry out the polymerization of the polymerization nature monomer which distributed a coloring agent in liquid data medium, and is distributed in [ after forming a globular form coloring particle ] liquid data medium as desiccation fine particles It found out that a toner particle which suited a nonmagnetic 1 component development method of above-mentioned this invention could be obtained easily.

[0019] Circumstances where it resulted in this invention, and details of invention are given below.

[0020] In order for this invention persons to improve image quality, such as definition, gradation nature, fogging, and image concentration In most fundamental place of an image formation method in connection with [ with last thing ] image formation equipment also in diameter[ of a granule ]-izing of a toner A result of having examined the condition wholeheartedly paying attention to setting it as conditions suitable for high definition-ization, As opposed to toner coating weight 0.5 on a developer support roll in a nonmagnetic 1 component developer by which current utilization is carried out — about two 0.7 mg/cm It found out that image quality could be raised remarkably by setting it as 0.2 — 0.4 mg/cm<sup>2</sup> still more desirably at 0.1 — 0.45 mg/cm<sup>2</sup>.

[0021] If there is much toner coating weight on a developer support roll, as a result of imprinting a superfluous toner on a printed object through a photo conductor, a fall of the definition of a printing image or gradation nature is caused. Moreover, when there is too little toner coating weight on a developer support roll, concentration of a printing image becomes inadequate and practicality is missing.

[0022] in order to boil image quality markedly and to raise it, it is required to control thickness of a toner layer on a printed object in a suitable range, and it is indispensable to set toner coating weight on a developer support roll as optimal range for that purpose. this invention persons succeeded in development of the technique of the ability to carry out stable manufacture of such a toner, and found out an image formation method which consists of the above-mentioned optimal coating weight which quality of an image is boiled markedly and can be further improved using the toner while they found out a fine-particles toner with the optimal property for improvement in such image quality.

[0023] In order to realize toner coating weight on a developer support roll concerning this invention, while making particle size of a toner small, in order to secure required particulate flow kinesis, a globular form is suitable for a toner configuration.

[0024] Particle size of a toner for this invention persons to adjust toner coating weight on a developer support roll to the aforementioned optimum value was made into volume mean particle diameter, and found out that it was [ 2-6-micrometer ] 3-5.5 micrometers still more desirably.

[0025] Although thickness of a toner layer of an image printed with the present fine-particles toner is very thick compared with thickness of an ink layer of a quality image printed in lithography ink etc., for image upgrading, it is important for it to make thickness of a toner layer of a printed image thinner than the present condition. If a toner is diameter[ of a granule ]-ized and toner coating weight on a developer support roll is decreased, in order that the

amount of toners which participates in image formation may decrease, a concentration fall of an image tends to take place. Then, coloring agent content of a toner is made to increase and it is necessary to secure required image concentration.

[0026] Therefore, in order to obtain printing image concentration sufficient with a diameter toner of a granule of 2-6micron which this invention makes an object, it is indispensable to set up pigment concentration in a toner above to some extent, and it may be necessary to make it commercial coloring agent concentration usually higher than a toner of size (7 micrometers - about 13 micrometers).

[0027] It is necessary to make it contain 9% of the weight or more still more desirably 8% of the weight or more to sum total weight of resin for binding, and a coloring agent in a black toner which used a carbon black pigment for a coloring agent in a 2-6-micrometer fine-particles toner of this invention. Moreover, it is necessary to make it contain 4% of the weight or more still more desirably 3% of the weight or more to sum total weight of resin for binding, and a coloring agent in a color toner which used an organic pigment for a coloring agent.

[0028] About a toner for black, control fixable by using styrene acrylic resin for resin for binding becomes easy, and it is suitable for this invention. Moreover, since coloring nature and gloss which were more excellent in using polyester resin for resin for binding are acquired about a color toner, it is suitable for this invention.

[0029] Average circularity (perimeter of a circle of the same area as particle projected area) (average of circularity defined by  $\frac{\text{perimeter of a particle projection image}}{\text{perimeter of a circle of the same area as particle projected area}}$ ) of a toner particle can attain easily conditions of toner coating weight on the above-mentioned developer support roll further again by using a fine-particles toner characterized by being 0.98 or more particles more preferably 0.97 or more. This is because a toner layer thin to homogeneity is easy to be formed on a developer support roll by moreover using a toner of a diameter of a granule in a globular form with such high sphericity.

[0030] Since a configuration of a toner particle crushing energy cost not only increases rapidly, but where mean particle diameter is obtained from about 6 micrometers is an indeterminate form when diameter[ of a granule ]-izing a fine-particles toner by the grinding method, frictional electrification nature and particulate flow kinesis of a toner which are acquired get worse. It is a big trouble when this puts a diameter toner of a granule about 6 micrometers or less in practical use.

[0031] However, in a 2-6-micrometer diameter toner of a granule which can improve greatly and this invention makes an object, 0.97 or more average circularity is required for a fall of particulate flow kinesis by diameter[ of a granule ]-izing of a toner by conglobating particle shape of a toner. although it asks by this average circularity's taking a SEM (scanning electron microscope) photograph of a toner particle, and measuring and calculating it etc. — the TOA Medical Electronics Co., Ltd. make — if flow type particle image analysis apparatus FPIP-1000 are used, it can measure easily.

[0032] Things and those [ this invention ] who have a main cause in further on the other hand some of coloring agents to contain and other additives (usually a wax, an electrification control agent, etc.) being exposed to the toner particle surface about aggravation of electrification nature by diameter[ of a granule ]-izing have guessed. That is, even if content (% of the weight) of a coloring agent etc. is the same, surface area of a toner particle increases by diameter-ization of a granule, and a ratio of a coloring agent exposed to the toner particle surface increases, consequently a presentation of the toner particle surface changes a lot, frictional electrification engine performance of a toner particle changes a lot, and control becomes difficult.

[0033] Even if it diameter[ of a granule ]-izes a toner, in order to hold frictional electrification engine performance good, it is effective to make it toner structure where the endocyst of making it not exposed [ a coloring agent etc. ] to the toner particle surface, i.e., the coloring agent etc., is carried out to a toner particle.

[0034] It can be easily judged by observing a cross section of a particle by TEM (transmission electron microscope) that neither a coloring agent, nor an electrification control agent (CCA), a wax, etc. are exposed to the toner surface. If required, when a cross section which carried out resin embedding of the toner particle, and was more specifically cut with a microtome will be dyed by ruthenium oxide etc. and will be observed by TEM, it is turned out clearly whether the endocyst of the coloring agent etc. is carried out to a particle.

[0035] Theoretically, although a diameter globular form toner of a granule (2-6micron) with which the endocyst of the above coloring agents etc. was carried out to a toner particle is possible, as for obtaining also by carrying out surface treatment of the particle of an indeterminate form made by the grinding method, and conglobating it by resin, it is practical to make from an ease, cost, etc. of manufacture with wet methods, such as a polymerization method and the emulsifying method, and it is suitable for it. Even if it changes a class of resin for binding broadly, it can form a good globular form coloring particle of particle size distribution, and since a rise of pigment concentration is easy for the emulsifying method, it is especially suitable especially as a process of a fine-particles toner of this invention.

[0036] Moreover, since particle size distribution of a toner which a way which used such a method describes below can also do a sharp thing, an effect to improvement in image quality becomes larger.

[0037] Although particle size distribution of a toner particle also affect electrification engine performance, particle size distribution especially with this invention more sharp than an about 7-13-micrometer toner by which current commercialization is carried out in the target diameter toner of a granule as knowledge are required. Namely, it sets to a fine-particles toner whose volume mean particle diameter which is the object of this invention is 2-6 micrometers. In measurement by coal tar multi-sizer, 50% volume particle size / 50% number particle size is 1.20 or less especially preferably 1.25 or less. And they are important requirements in order to obtain a quality printing image which it discovers good electrification nature that a square root of volume particle size has 1.20 or less

particle size distribution more preferably 1.25 or less 84% volume particle size / 16%, and does not have fogging.

[0038] Moreover, a uniformity coefficient of an array of a toner on a development roll is considered that it can cover a development roll with increase and a more nearly little toner in this way by using a toner particle with sharp particle size distribution of a toner of a diameter of a granule in a globular form.

[0039] Exceptional remarkable efficacy that using a globular form toner of a diameter of a granule with such narrow particle size distribution leads not only to improvement in image quality but to sharp reduction of toner consumption per printing is demonstrated. By reducing toner consumption per printing, cost of printing/copy is reduced and a merit of being able to miniaturize toner box capacity of a machine is also produced.

[0040] Furthermore, frictional electrification nature and particulate flow kinesis of a diameter toner of a granule can be improved also by choosing appropriately a class and an amount of an inorganic oxide particle which are added and used for the toner surface. As an inorganic oxide particle which can be used for this invention, a silica (oxidation silicon), titanium oxide, an aluminum oxide, a zinc oxide, tin oxide, antimony oxide, a magnesium oxide, etc. are mentioned, for example. Independent use or two or more sorts of concomitant use are sufficient as these.

[0041] Also among these, especially a silica whose diameter of a primary particle is about 5-50nm and by which hydrophobic processing was carried out is suitable, and it is also suitable for a silica to use it if needed, combining with other inorganic oxide particles. Many hydrophobic silicas for toners are marketed and it is convenient practically to use it, choosing from them.

[0042] As an addition of an inorganic oxide particle, although it changes with purposes of using a fine-particles toner, it is desirable that a thing which has a small toner particle size more generally makes [ many ] an addition. It is suitable to \*\* an amount shown by degree type to a particle (C) outside by 2-6-micrometer toner particle of this invention.

[0043]

[Formula 3]

$3.5714X - 0.9942 \leq Y \leq 31.399X - 0.9477$  [0044] It is outside \*\*\*\* [ as opposed to / Y / as opposed to / in X / 50% volume particle size (micrometer) of a particle (C) / among [type / \*\*\*\* / a particle (C)] (% of the weight). ]

[0045] What is necessary is just to perform \*\* by method of well-known common use using a Henschel mixer, high BURIDAZA, etc. outside these.

[0046] That is, the electrification nature of a toner and a fluidity are remarkably improvable by using a toner which fulfilled the above-mentioned conditions.

[0047] As mentioned above, although it is characterized by setting toner coating weight on a developer support roll as the range of two or less 0.45 mg/cm by two or more 0.1 mg/cm and this can attain upgrading of a remarkable image by nonmagnetic 1 component development method of this invention toner coating weight — this range — setting up — in addition — and in order to have better image quality, it is necessary to set up more desirable conditions about a presentation, a process, etc. also about said toner used as carried out

[0048] The details of a suitable presentation and a suitable process of a toner used for below by the image formation method of these this inventions are given.

[0049] As a coloring agent used for a fine-particles toner of this invention, there is especially no limit, it can use conventionally a coloring agent used with a toner for electrophotography etc., and its pigment is desirable and it can illustrate the following.

[0050] As a black pigment, carbon black, cyanine black, aniline black, a ferrite, magnetite, etc. are mentioned, for example. Or carbon black is more suitable although what prepared the following chromatic color pigments so that it might become black can be used.

[0051] As a yellow pigment, for example The chrome yellow, zinc yellow, cadmium yellow, Synthetic Ochre, Ocher, Titanium Yellow, Naphthol Yellow S, Hansa yellow 10G, Hansa yellow 5G, Hansa yellow G, Hansa yellow GR, Hansa yellow A, Hansa yellow RN, Hansa yellow R, the pigment yellow L, benzidine yellow, benzidine yellow G Benzidine yellow GR, the permanent yellow NCG, Balkan Peninsula first yellow 5G, The Balkan Peninsula first yellow R, a quinoline yellow lake, ANSURA gene yellow 6GL, The permanent yellow FGL, permanent yellow H10G, the permanent yellow HR ANSURA pyrimidine yellow, other isoindolinone yellow, chromophthal yellow, NOBOPAMU yellow H2G, condensation azo yellow, Nickel Azo Yellow, copper azomethine yellow, etc. are mentioned.

[0052] As red pigments, for example The red chrome yellow, a molybdenum orange, permanent Orange GTR, Pyrazolone Orange, Balkan Peninsula Orange, INDAN Indanthrene brilliant Orange RK, INDAN Indanthrene brilliant Orange GK, a benzidine orange G, Permanent Red 4R, Permanent Red BL, Permanent Red F5RK, Lithol Red, Pyrazolone red, WOTCHINNGUREDDO, Lake Red C, Lake Red D Brilliant carmine 6B, brilliant carmine 3B, the rhodamine lake B an alizarin lake and permanent carmine FBB — a non orange, isoindolinone Orange, ANSU anthrone Orange, pyran SURON Orange, the Quinacridone red, the Quinacridone Magenta, Quinacridone Scarlett, perylene red, etc. are very mentioned.

[0053] As a blue pigment, cobalt blue, cerulean blue, an alkali blue lake, a peacock blue lake, FANA tone blue 6G, a Victoria blue lake, non-metal copper phthalocyanine blue, copper copper phthalocyanine blue, Fast Sky Blue, INDAN Indanthrene blue RS, INDAN Indanthrene blue BC, indigo, etc. are mentioned, for example.

[0054] The way of making depended on a method of emulsifying a toner particle used for this invention is as follows. this particle that is made to mix and emulsify an organic solvent solution which uses a coloring agent and resin for binding of nonaqueous solubility as an indispensable component, and aqueous data medium, removes an organic solvent after forming a globular form coloring resin particle, and is distributed in aqueous data medium — as desiccation fine particles — ejection and necessity — that — \*\*\*\*\* is performed, particle size distribution are

prepared and a toner particle is made.

[0055] As said organic solvent used for distributions, such as dissolution of resin for binding, and a coloring agent For example, a pentane, a hexane, a heptane, benzene, toluene, a xylene, Hydrocarbons, such as a cyclohexane and the petroleum ether; A methylene chloride, chloroform, A dichloroethane, a dichloroethylene, trichloroethane, a trichloroethylene, Halogenated hydrocarbon, such as a carbon tetrachloride; A methanol, ethanol, Alcohols, such as isopropyl alcohol, n-propyl alcohol, and a butanol; An acetone, Ketones, such as a methyl ethyl ketone and methyl isobutyl ketone; ester, such as ethyl acetate and butyl acetate, is mentioned, and these two or more sorts may be mixed and used.

[0056] Although it will be good and there will be especially no limitation as said resin for binding if meltable to the above-mentioned organic solvent, in itself, there are nonaqueous solubility resin which does not distribute to aqueous data medium but may be distributed to aqueous data medium for the first time using an emulsifier or a distributed stabilizer, and nonaqueous solubility resin which may be distributed to aqueous data medium by itself and which has "self-water-dispersion."

[0057] As such nonaqueous solubility resin for toners, there is styrene resin, acrylic (meta) resin, polyester system resin, polyurethane system resin, or epoxy system resin, for example. The so-called styrene (meta) acrylic resin by which the polymerization was carried out especially by using a styrene system monomer and acrylic ester (meta) as an indispensable component is suitable. In this invention, a meta-acrylic and an acrylic are included by acrylics (meta).

[0058] It is usually 3000-300000 as weight average molecular weight, and molecular weight of level required to discover sufficient mechanical strength as said resin and a thing whose glass transition temperature (T<sub>g</sub>) is 50-100 degrees C are suitable in DSC (differential scanning calorimeter) measurement.

[0059] Among said resin for binding, self-water-dispersion resin is resin containing a functional group which can serve as an anion mold by neutralization, and resin which can form a water dispersing element stabilized under an operation of aqueous data medium by which a part or all of a functional group that can serve as these hydrophilicity was neutralized by base, without using an emulsifier or a distributed stabilizer is said.

[0060] As a functional group which can turn into a hydrophilic radical by neutralization, the so-called acidic groups, such as a carboxyl group, a phosphate group, and a sulfonic group, are mentioned, for example. As resin containing these functional groups, styrene resin, acrylic (meta) resin, polyester system resin, polyurethane system resin, epoxy system resin, etc. are mentioned. Thus, styrene (meta) acrylic resin which has an acidic group is used suitably.

[0061] What is made to carry out the radical polymerization of the polymerization nature vinyl monomer represented by acrylic ester (meta) other than the acrylic (meta) polymerization nature vinyl monomers which contained an acid radical by using a styrene system monomer as an indispensable component as suitable anion mold styrene (meta) acrylic resin which can serve as self-water-dispersion by neutralization to use by this invention, and the polymerization nature vinyl monomers containing this acid radical under radical initiator existence, and is obtained can be used. A polymerization reaction for obtaining it can be suitably used also by solution polymerization or suspension, and emulsion polymerization.

[0062] As such acid radical content (meta) acrylic polymerization nature monomers, an acrylic acid, a methacrylic acid, a crotonic acid, an itaconic acid, a maleic acid, a fumaric acid, itaconic-acid monobutyl, maleic-acid monobutyl, etc. are mentioned, for example.

[0063] As polymerization nature monomers other than acid radical content polymerization nature monomers, there is styrene, vinyltoluene, 2-methyl styrene, t-butyl styrene, or KURORU styrene, for example as styrene system monomers (aromatic series vinyl monomer).

[0064] As acrylic ester, a methyl acrylate, an ethyl acrylate, acrylic-acid isopropyl, acrylic-acid n-butyl, isobutyl acrylate, acrylic-acid n-amyl, acrylic-acid isoamyl, acrylic-acid n-hexyl, 2-ethylhexyl acrylate, acrylic-acid n-octyl, acrylic-acid DESHIRU or acrylic-acid dodecyl, acrylic-acid 2-KURORU ethyl, acrylic-acid phenyl, and alpha KURORUA krill acid methyl are mentioned, for example.

[0065] As methacrylic ester, a methyl methacrylate, methacrylic-acid propyl, n-butyl methacrylate, methacrylic-acid isobutyl, methacrylic-acid n-amyl, methacrylic-acid n-hexyl, 2-ethylhexyl methacrylate, n-octyl methacrylate, methacrylic-acid DESHIRU, methacrylic-acid dodecyl, methacrylic-acid 2-KURORU ethyl, methacrylic-acid phenyl, and alpha clo RUMETA krill acid methyl are mentioned, for example.

[0066] Moreover, N-vinyl compounds, such as vinyl ketones, such as vinyl ether, such as acrylic acids, such as acrylonitrile, meta-acrylonitrile, and acrylamide, or a methacrylic-acid derivative, vinyl methyl ether, vinyl ethyl ether, and the vinyl isobutyl ether, a vinyl methyl ketone, a vinyl hexyl ketone, and a methyl isopropenyl ketone, N-vinyl pyrrole, N-vinylcarbazole, N-vinyl indole, and N-vinyl pyrrolidone, etc. can be mentioned.

[0067] Moreover, it faces obtaining resin which can serve as self-water-dispersion by neutralization, and, in the case of solution polymerization, a general-purpose organic solvent can be used. Specifically, they are the so-called inactive solvents, such as various kinds of ether ester like various kinds of ester; like various kinds of ketones; ethyl acetate or butyl acetate like various kinds of ether alcohol; acetones [ like / various kinds of alcohols; cellosolves or carbitols like various kinds of aromatic hydrocarbon; methanols / like / toluene, a xylene, or benzene /, ethanol, propanol, or a butanol ], a methyl ethyl ketone, or methyl isobutyl ketone, or butyl-cellosolve acetate.

[0068] Moreover, as a polymerization initiator to be used, an initiator of various kinds of organic peroxide systems of well-known common use and an initiator of an azo system can be used. Specifically, azo system compounds, such as peroxides, such as benzoyl peroxide, cumene hydronalium peroxide, t-butyl hydroperoxide, sodium persulfate, and ammonium persulfate, azobisisobutyronitril, and azobisiso valeroneitrile, are mentioned.



[0069] Although especially a content of a carboxyl group of carboxy group content anion mold resin which can serve as a hydrophilic radical by neutralization is not restricted, they are the acid numbers (mg of KOH required to neutralize 1g of resin number) 30-150 preferably in styrene resin, acrylic (meta) resin, and suitable styrene (meta) acrylic resin.

[0070] In this invention, although polyester system resin of well-known common use can be used, it can use a thing to which polyhydric alcohol, and polybasic acid or its ester plasticity derivative was made to react.

[0071] Under existence of a solvent or nonexistence, under existence of a catalyst, suitable polyester resin to use by this invention performs a dehydration polycondensation, and can manufacture polybasic acid and polyhydric alcohol of a raw material. A part of polybasic acid may perform a demethanol polycondensation using the methyl ester ghost which is one of the ester plasticity derivatives of that.

[0072] More specifically, aromatic polyester system resin to which aromatic series dicarboxylic acid or its ester plasticity derivative like a phthalic acid was made to react as an indispensable component is desirable. Melttable resin for binding is used for a solvent used for it at the emulsifying method.

[0073] As an example of polybasic acid to be used, alicyclic carboxylic acids, such as aliphatic carboxylic acid, such as aromatic carboxylic acid, such as a terephthalic acid, isophthalic acid, phthalic anhydride, trimellitic anhydride, pyromellitic acid, and naphthalene dicarboxylic acid, a maleic anhydride, boletic acid, a succinic acid, an alkenyl succinic anhydride, and an adipic acid, and cyclohexane dicarboxylic acid, are mentioned, for example. these polybasic acid — one sort — or two or more sorts can be used.

[0074] As an example of polyhydric alcohol to be used, aromatic series system diols, such as alicyclic diols, such as aliphatic series diols, such as ethylene glycol, propylene glycol, butanediol, hexandiol, neopentyl glycol, and a glycerol, cyclohexane diol, cyclohexane dimethanol, and hydrogenation bisphenol A, an ethyleneoxide addition product of bisphenol A, and a propylene oxide addition product of bisphenol A, are mentioned, for example. one sort of these polyhydric alcohol — or two or more sorts can be used.

[0075] A glass transition point of polyester resin is 55-70 degrees C preferably [ that it is 50-75 degrees C ] and more preferably. Since the heat-resistant coherent one as a toner becomes that a glass transition point is less than 50 degrees C poor, and fixable will become poor if 75 degrees C is exceeded, it is not desirable.

[0076] The above-mentioned polybasic acid, a compounding ratio of polyhydric alcohol, and conversion can adjust a content of an acid radical of polyester by controlling a carboxyl group of an end of polyester. Or what has a carboxyl group in a principal chain of polyester is obtained by using trimellitic anhydride as a polybasic acid component. 1 - 30 mg-KOH/g is suitable for a content of an acid radical of polyester system resin as the acid number.

[0077] As a basic neutralizer used for these, although there is especially no limitation, organic bases, such as inorganic alkali, such as a sodium hydroxide, a potassium hydroxide, a lithium hydroxide, a calcium hydroxide, a sodium carbonate, and ammonia, and diethylamine, triethylamine, isopropylamine, are mentioned, for example.

[0078] To use nonaqueous solubility resin which does not distribute namely, have self-water-dispersion in water by itself which was described above as nonaqueous solubility resin which is resin for binding, it is required to add and use an emulsifier and/or a distributed stabilizer for aqueous data medium (for aqueous data medium to say a solvent object which used water or water as a principal component) mixed with a resin solution and/or it.

[0079] As the distributed stabilizer, a water soluble polymer compound is desirable, for example, polyvinyl alcohol, a polyvinyl pyrrolidone, hydroxyethyl cellulose, a carboxymethyl cellulose, etc. are mentioned. Moreover, as an emulsifier, various surfactants of anion systems, such as the Nonion systems, such as the PORIOKI ethylene alkylphenol ether, and alkyl benzene sodium sulfonate, or a cation system are mentioned, for example. Of course, although two or more sorts of an emulsifier may be used together, two or more sorts of a distributed stabilizer may be used together and an emulsifier and a distributed stabilizer may be used together, it is common to make a distributed stabilizer into a subject and to use an emulsifier together.

[0080] In this case, when using an emulsifier and a distributed stabilizer, it is appropriate for concentration in that aqueous data medium to make it become about 0.5 - 3 % of the weight.

[0081] Furthermore, unless an effect of this invention will be spoiled if required even if it is the case where resin which can serve as self-water-dispersion by [ which were mentioned above ] neutralizing is used, an emulsifier and /\*\* may use a distributed stabilizer.

[0082] To the target globular form coloring resin particle, this invention may add waxes (release agent), such as electrification control agents (CCA), such as a metal-containing azo compound and a salicylic-acid system metal complex, and polyethylene wax, a polypropylene wax, paraffin wax, and an additive which is a silicone oil etc. further about 0.1 to 10% of the weight to resin for binding if needed.

[0083] About addition of these additives and said coloring agents, it is good by methods, such as using general mixing and disperser like a ball mill after adding these, or a continuous system bead mill for an organic solvent solution of resin for binding, and making it fully grind and mix etc.

[0084] Thus, dispersion liquid of a globular form coloring resin particle obtained by emulsification obtain a original object particle by carrying out aqueous dispersion liquid a \*\* exception with means, such as filtration, and drying a particle, after removing an organic solvent first with means, such as distillation. As for a coloring resin particle obtained using an emulsifier or a distributed stabilizer, it is desirable to more fully wash and to use.

[0085] Of course, become an anionic hydrophilic radical by neutralization as resin for binding. [ when obtaining a resin particle by this invention using self-water-dispersion resin which neutralized and obtained nonaqueous solubility resin which has an acidic group with a basic neutralizer ] After removing an organic solvent beforehand, with acid neutralizers, such as a hydrochloric acid, a sulfuric acid, phosphoric acid, an acetic acid, and oxalic acid

Since reverse neutralization processing in which a hydrophilic radical which was neutralized as a basic compound on the surface of a particle is also, and was obtained is returned to a functional group of a basis is performed and the hydrophilicity of the particle itself is reduced more, it is desirable to adopt a method of removing water and drying a \*\* exception.

[0086] Although each a method of well-known common use can adopt said desiccation, toner particles are heat welding and the temperature which is not condensed, and you may dry under ordinary pressure or reduced pressure, for example, and a method of freeze-drying is also mentioned. Moreover, there is also a method of performing separation and desiccation of a toner particle from aqueous data medium to coincidence using a spray dryer etc. While a toner particle heats at heat welding or temperature which is not condensed especially, it is efficient to agitate fine particles and to dry under reduced pressure, and it is desirable.

[0087] In order to prepare particle size distribution of a toner particle, when a classification for removing a big and rough particle and a very fine particle is required, you may carry out by method of well-known common use using a common dry classifier marketed for toners etc., and may carry out using a difference in sedimentation nature by particle size by method of classifying a water slurry of a globular form coloring particle using a centrifugal separator. Moreover, removal of a big and rough particle can be efficiently performed also by filtering a water slurry of a globular form coloring particle using a filter.

[0088] The way of making depended on a polymerization method of a toner particle used for this invention is as follows. a polymerization nature monomer which distributed a coloring agent — a solvent — a polymerization is carried out in a body — making — a solvent after forming a globular form coloring resin particle — this particle currently distributed inside of the body — as desiccation fine particles — ejection and necessity — that — \*\*\*\*\* is performed, particle size distribution are prepared and a toner particle is made.

[0089] a reactant monomer which can specifically form a coloring agent and binder resin in the bottom of existence of a distributed stabilizer and an emulsifier — a solvent — suspension or a polymerized reaction [ stirring under existence of a polymerization initiator by carrying out emulsification distribution ] by radical polymerization can be performed inside of the body, and aqueous dispersion liquid of a toner particle which connoted a coloring agent in globular form resin for binding can be obtained.

[0090] As the above-mentioned radical polymerization nature monomer, specifically For example, styrene, such as styrene, alpha methyl styrene, chloro styrene, and vinylstyrene Monoolefins, such as ethylene, a propylene, a butylene, and an isobutylene Vinyl ester, such as vinyl acetate, propionyl vinyl, butanoic acid vinyl, and benzoic-acid vinyl A methyl acrylate, an ethyl acrylate, butyl acrylate, acrylic-acid octyl, Acrylic-acid dodecyl acrylic-acid phenyl, a methyl methacrylate, ethyl methacrylate methacrylic-acid butyl, alpha-methylene aliphatic series monocarboxylic acid ester, such as methacrylic-acid dodecyl Ethylene glycol monoacrylate, a propylene glycol mono-bitter taste lied, Glycol monochrome (meta) acrylic ester, such as tetramethylen ether glycol monoacrylate, Vinyl ether, such as vinyl methyl ether, vinyl ethyl ether, and vinyl butyl ether Acrylic monomers, such as vinyl ketones, such as a vinyl methyl ketone, a vinyl hexyl ketone, and a vinyl propenyl ketone, are mentioned, and these are independent, respectively or can be used combining two or more kinds.

[0091] A monomer presentation which constitutes the binder resin is prepared so that glass transition temperature ( $T_g$ ) of a polymer may become 50–80 degrees C.

[0092] A reactant monomer which has two or more little ethylene nature partial saturation double bonds may be used together to it if needed. As a reactant monomer which has two or more ethylene nature partial saturation double bonds, conjugated dienes, such as a butadiene and an isoprene, a divinylbenzene, di(meth)acrylate of the bisphenol A alkylene oxide addition product, TORIMECHI roll pro pantry (meta) acrylate, pentaerythritol tetrapod (meta) acrylate, etc. are mentioned, for example.

[0093] In addition, as a polymerization initiator used for obtaining such polymer resin, of course, although a thing the usual oil solubility or water-soluble can be used, various kinds of azo compounds [ like / various kinds of peroxides; like a benzoyl peroxide, G t-butyl peroxide cumene hydroperoxide, t-butyl peroxide, or 2-ethylhexanoate, azobisisobutyronitril, or azobisiso valeronitrile ] etc. can mention, for example.

[0094] On the occasion of a suspension polymerization, an insoluble and monomer soluble polymerization initiator is chosen as a solvent object used for a polymerization as indispensable, and is used for it, and a water-soluble polymerization initiator is used on the occasion of an emulsion polymerization, choosing as indispensable. Although especially the amount of polymerization initiator used is not restricted, it is per overall reaction nature monomer (total monomer) weight 100 weight section and 0.01 – 5 weight section.

[0095] Although resin for binding formed of a polymerization can be prepared to arbitration according to polymerization conditions etc., it is desirable as weight average molecular weight to make it set to 10,000–500,000.

[0096] A coloring agent in this toner particle, an electrification control agent, a wax, etc. are the same as that of a case of said emulsifying method toner, and a thing of well-known common use can be used for them.

[0097] As said distributed stabilizer which can be used at the time of a suspension polymerization, generally, a water soluble polymer compound is used, for example, polyvinyl alcohol, a polyvinyl pyrrolidone, hydroxyethyl cellulose, a carboxymethyl cellulose, cellulose gum, ram ZANGAMU, etc. are mentioned.

[0098] Non-subtlety powder whose particle size is furthermore 0.01–5 micrometers by water-insoluble nature can also be used as a suspension distribution stabilizer, for example, tricalcium phosphate, talc, a bentonite, a kaolin, titanium oxide, an alumina, a zinc white, an aluminum hydroxide, a magnesium hydroxide, a basic magnesium silicate, hydroxylation titanium, a ferric hydroxide, a barium sulfate, a silica, a magnesium carbonate, a calcium carbonate, etc. are mentioned.

[0099] Independent use is sufficient as a distributed stabilizer, and two or more sorts of concomitant use is sufficient as these. The amount used is usually 0.1 – 10 weight section per overall reaction nature monomer 100 weight section.

[0100] As said emulsifier which can be used for an emulsion polymerization, nonionic surfactants, such as anionic surfactants, such as sodium dodecylbenzenesulfonate, sodium lauryl sulfate, and dodecyl diphenyloxide disulfon acid sodium, the polyoxyethylene lauryl ether, and the polyoxyethylene nonyl phenol ether, etc. can be mentioned, for example. Independent use is sufficient as these and two or more sorts of concomitant use is sufficient as them. The amount used is usually 0.01 – 5 weight section per overall reaction nature monomer 100 weight section.

[0101] In a suspension polymerization, a part of emulsifier may be used together to a distributed stabilizer, and a part of distributed stabilizer may be used together to an emulsifier in an emulsion polymerization. Moreover, it can replace with the above-mentioned distributed stabilizer or an emulsifier, and a self-emulsifiability epoxy resin and self-emulsifiability polyurethane resin can also be used.

[0102] a polymerization nature monomer, a coloring agent, a distributed stabilizer, and said monomer — a polymerization initiator [ insoluble on an insoluble solvent object and said solvent object and ] meltable to said monomer — coincidence — in addition Although it may stir and the polymerization of the monomer drop may be carried out, a polymerization nature monomer and a coloring agent for example, by ball mill, a colloid mill, etc. Fully mix beforehand and, subsequently it is added to said solvent object containing a polymerization initiator and a distributed stabilizer. For example, stirring by homogenizer, rotor stator type mixer, a static mixer, etc., carrying out suspension of the monomer drop which makes a polymerization nature monomer indispensable into liquid data medium, and continuing stirring, it is desirable to perform a polymerization until a toner particle of predetermined particle diameter is formed.

[0103] As a solvent object which can be used in performing such a polymerization Like a xylene, others, for example, toluene, or benzene [ water /, such as distilled water and ion exchange water, ] Various kinds of aromatic hydrocarbon; like a methanol, ethanol, propanol, or a butanol Various kinds of alcohols; Various kinds of ether alcohol; acetones [ like / cellosolve or carbitol ], Various kinds of ketones like a methyl ethyl ketone or methyl isobutyl ketone; various kinds of ether ester like various kinds of ester; like ethyl acetate or butyl acetate or butyl-cellosolve acetate is mentioned.

[0104] In addition, also in which polymerization method, change can also be given to the chemical structure, layer structure, etc. of a particle by adopting a core shell polymerization formula, a power feed polymerization formula, and a graft polymerization formula. It is not restricted, and also in which method, especially a reaction condition in each suspension-polymerization method and an emulsion-polymerization method of each above-mentioned invention is usually room temperature –80 degree C, and is 15 minutes – 24 hours.

[0105] Thus, dispersion liquid of an obtained globular form coloring resin particle can remove a solvent object, and can obtain fine particles of a globular form coloring resin particle easily by drying. In addition, in order to remove a distributed stabilizer and an emulsifier in said dispersion liquid, it is desirable to repeat washing and to perform it. In carrying out solvent object removal / desiccation production process, hot air drying can be carried out at temperature to which this particle does not weld a globular form coloring resin particle the back according to \*\*, or it can also freeze-dry, and a spray dryer etc. may be made to perform solvent object removal and desiccation to coincidence. As for desiccation, it is efficient to carry out stoving, agitating a toner particle under reduced pressure.

[0106] in order [ in addition, ] to prepare particle size distribution of a toner particle — necessity — that — the same classification actuation as a case of the \*\*\*\*\* method toner can be performed.

[0107] Thus, while being able to set easily toner coating weight on a developer support roll which is this invention by using an obtained toner as the range or less [ 0.45mg //cm ] of two from two or more 0.1 mg/cm, it excels in resolution and gradation nature of an image, and image concentration can acquire outstanding image quality with little fogging highly.

[0108]

[Embodiment of the Invention] This invention includes the following operation gestalten.

[0109] 1. Nonmagnetic 1 component development method characterized by toner coating weight on developer support roll being range of two or more to two or less 0.45 mg/cm using globular form toner whose volume mean particle diameter is 2–6 micrometers as developer in nonmagnetic 1 component development method which supplies developer to photo conductor and actualizes electrostatic latent image on photo conductor using nonmagnetic 1 component developer which has developer support roll and stratification member at least. [ 0.1 ]

[0110] 2. Nonmagnetic 1 component development method of one above-mentioned publication using globular form toner whose content of this carbon black coloring agent is 8 % of the weight or more in carbon black as developer at styrene (meta) acrylic resin for resin for binding.

[0111] 3. Nonmagnetic 1 component development method of one above-mentioned publication using globular form toner whose content of this organic pigment coloring agent is 3 % of the weight or more in organic pigment as developer at polyester resin for resin for binding.

[0112] 4. Nonmagnetic 1 component development method the above 1 and 2 using 0.97 or more globular form toners of average circularity by which endocyst of coloring agent was carried out to resin for binding as developer, or given in three.

[0113] 5. Image formation method the above 1, 2, and 3 50% volume particle size / whose 50% number particle size particle size distribution of globular form toner used as developer are 1.25 or less and whose square roots of 84%

volume particle size / 16% volume particle size are 1.25 or less, or given in four.

[0114] 6. Nonmagnetic 1 component development method the above 1, 2, 3, and 4 by which only amount inorganic oxide particle is indicated to be by degree type is \*(ed) outside by globular form toner particle used as developer, or given in five.

[0115]

[Formula 1]

$3.5714X - 0.9942 \leq Y \leq 31.399X - 0.9477$  — [ — outside \*\*\*\* [ as opposed to / Y / here / as opposed to / in X / the volume mean particle diameter (micrometer) of a toner particle / \*\*\*\* / a toner particle ] (% of the weight). ]

[0116] 7. a toner particle mixes and emulsifies the organic solvent solution which uses a coloring agent and the resin for binding of nonaqueous solubility as an indispensable component, and aqueous data medium — making — the solvent after forming a globular form coloring particle — the nonmagnetic 1 component development method the above 4 and 5 obtained by the method of taking out this particle currently distributed inside of the body as desiccation fine particles, or given in six.

[0117] 8. the polymerization nature monomer which the toner particle made distribute a coloring agent — a solvent — a polymerization is carried out in a body — making — the solvent after forming a globular form coloring particle — the nonmagnetic 1 component development method the above 4 and 5 obtained by the method of taking out this particle currently distributed inside of the body as desiccation fine particles, or given in six.

[0118]

[Example] Next, the example of reference, an example, and the example of a comparison explain this invention concretely. All of the section and % are weight criteria.

[0119] (Example 1 of reference) After teaching the 667 sections of a methyl ethyl ketone and carrying out the temperature up to 80 degrees C, the mixture which consists of following monomers and a following polymerization initiator was dropped at the 3l. flask equipped with the synthetic example dropping equipment, the thermometer, the nitrogen gas installation pipe, the churning equipment, and the reflux condenser of styrene-acrylic resin of carboxyl group content over 2 hours. The reaction was performed under the nitrogen gas air current.

[0120]

styrene 668 section butyl acrylate 223 section acrylic acid The 109 sections "par butyl O" the 50 sections — the occasion — after carrying out dropping termination, 3 times "par butyl O" (radical polymerization initiator by Nippon Oil & Fats [ Co., Ltd. ] Co., Ltd.) of the three sections were added every 3 hours, and after continuing the reaction for further 4 hours, it ended. Desolventization was performed after that and hard resin (R-1) was obtained. The glass transition temperature of this resin was [ 20000 and the acid number of 72 degrees C and weight average molecular weight ] 81.

[0121] (Example 2 of reference) After teaching the 114/12/24 section of a methyl ethyl ketone / isopropyl alcohol / water to the 3l. flask equipped with the synthetic example dropping equipment, the thermometer, the nitrogen gas installation official, the churning equipment, and the reflux condenser of styrene-acrylic resin of carboxyl group content, the temperature up was carried out to 80 degrees C, the mixture which consists of the monomers and polymerization initiator of presentation 1 was prepared collectively, and the reaction was started.

[0122]

Presentation 1 Styrene The 330 sections Butyl acrylate The 216 sections Acrylic acid The 54 sections "Par butyl O" The 0.6 sections [0123] Subsequently, the about 10 sections of a reaction resin solution were sampled every other hour 3 hours after, it diluted with the methyl ethyl ketone of tales doses, and viscosity was measured with the Gardner viscometer. When viscosity became P-Q, after it added the 567/63 section of a methyl ethyl ketone/isopropyl alcohol and temperature became 80 degrees C, mixture as shown in presentation 2 was dropped over 1 hour. In addition, it was 60% when the 1st step of conversion was calculated by carrying out the quantum of the monomer survival rate at this time with a gas chromatography.

[0124]

Presentation 2 Styrene The 413 sections Butyl acrylate The 133 sections Acrylic acid The 54 sections "Par butyl O" The 18 sections [0125] 3 times "par butyl O" of the two sections were added every 3 hours after dropping termination, and after continuing the reaction for further 4 hours, it ended. Then, desolventization was performed and hard resin (R-2) was obtained. The glass transition temperature of this resin was [ 124000 and the acid number of 61 degrees C and weight average molecular weight ] 70.

[0126] (Example 1 of toner manufacture) 1 hour made the 2000 sections of R-2, and the 500 sections of carbon black (ELFTEX8 by Cabot Corp.) knead using a kneader. The rate of the resin solid content / pigment of this masterbatch becomes 80/20. This masterbatch 750 section, the hard resin 450 section of R-2, and the hard resin 300 section of R-1 The 150 sections of wax dispersing element "H808" (the emulsion mold wax by the Chukyo fats-and-oils company, the Fischer Tropsch wax, particle diameter of 0.5 micrometers, 30% of solid content contents) are added in the carbon distribution resin solution which dissolved in the 1000 sections of a methyl ethyl ketone, next was obtained, and it is "Eiger motor mill. M-250" was used and it was made to mix and distribute for 10 minutes. Subsequently, nonvolatile matter concentration was adjusted to 53% by the methyl ethyl ketone, and the mill base was produced.

[0127] Subsequently, holding and stirring inside \*\* at 30 degrees C, the deionized water 43 section is dropped, phase inversion emulsification was carried out, and the resin particle was made to form, after adding the 48 sections of the sodium-hydroxide aqueous solution of 1 convention, the 58 sections of isopropyl alcohol, and the 150 sections of deionized water and mixing well to the 566 sections of this mill base. Furthermore, the 500 sections of

deionized water were added after 30 minutes.

[0128] Next, after removing an organic solvent and carrying out a resin particle a \*\* exception [ data medium / water ] by vacuum distillation, this particle was made to re-distribute underwater. Then, after 0.1-N hydrochloric-acid aqueous solution adjusted these dispersion liquid to pH2 and stirring them for 30 minutes, this water slurry was processed with the centrifugal separator, fines were removed, subsequently to a filter (product made from Chisso Filter) the water slurry was passed, and the big and rough particle was removed. After carrying out actuation which carries out re-distribution washing underwater further after carrying out a water slurry a \*\* exception, made the resin particle separate from water data medium, obtained the wet cake, this was made to freeze-dry, and it considered as the powder of a black resin particle.

[0129] The volume mean particle diameter of the obtained black resin particle was 5.0 micrometers by the measurement which used the coal tar Marti sizer 2, and 50% volume particle size / 50% number particle size was the good particle size distributions [ square root / of 1.10 or 84% volume particle size / 16% volume particle size ] 1.21. the TOA Medical Electronics Co., Ltd. make -- when measured by flow type particle image analysis apparatus FPIP-1000, average circularity was the globular form of 0.989. When the cross section which carried out resin embedding of this particle, and was cut with the microtome was observed by TEM (transmission electron microscope), the endocyst of the carbon black pigment was carried out to the particle, and it was distributed to homogeneity.

[0130] To this fine-particles 100 section, it is the 1.3 sections and hydrophobic silica Wacker of titanium oxide particle MT-150 (TAYCA make). HDK The 1.9 sections of SLM50650 were \*\* (ed) outside using the Henschel mixer, and the globular form fine-particles toner 1 was prepared.

[0131] (Example 2 of toner manufacture) After adding the 54 sections of the sodium-hydroxide aqueous solution of 1 convention, the isopropyl alcohol 52 section, and the 130 sections of deionized water and mixing well to the 566 sections of the mill base, the black resin particle powder made into the purpose was obtained by the same actuation as an example 1 except the deionized water 21 section having been dropped and having carried out phase inversion emulsification, holding and stirring inside \*\* at 30 degrees C.

[0132] The volume mean particle diameter of the resin particle powder obtained here was 3.2 micrometers, and 50% volume particle size / 50% number particle size was the good particle size distributions [ square root / of 1.11 or 84% volume particle size / 16% volume particle size ] 1.20. Average circularity was the globular form of 0.990, when TEM observation of this particle cross section was carried out, the endocyst of the carbon black pigment was carried out to the particle, and it was distributed to homogeneity.

[0133] In this fine-particles 100 section, the 1.5 sections of titanium oxide particle MT-150 and the 2.5 sections of the hydrophobic silica SLM50650 were \*\* (ed) outside, and the globular form fine-particles toner 2 was prepared in it.

[0134] (Example 3 of toner manufacture) Except having made content to the resin for binding of carbon black into 6%, it corned on the same conditions as the example 1 of toner manufacture, and volume mean particle diameter obtained 5.0 micrometers and the black resin particle fine particles in which number particle size has the good particle size distribution [ square root / of volume particle size ] 1.18, 50% volume particle size / 50% 1.09 or 84% volume particle size / 16%. Average circularity was 0.989, when TEM observation of the particle cross section was carried out, the endocyst of the carbon black pigment was carried out to the particle, and it was distributed to homogeneity. The same outside \*\* as an example 1 was given to these fine particles, and the globular form fine-particles toner 3 was prepared to them.

[0135] (Example 4 of toner manufacture) The 800 sections of a methyl ethyl ketone were added to the polyester resin 1200 section whose melt viscosity [ in / 4 mg-KOH/g and weight average molecular weight, and / in a glass transition point / 61 degrees C and 100 degrees C ] is 40000poise, and the acid number added the phthalocyanine pigment "Ket Blue 123" (Dainippon Ink & Chemicals make) 76.5 section to the resin solution which dissolved well, carried out churning mixing, and fully distributed. [ 12000 ] The methyl ethyl ketone adjusted the solid content content to 50% after distributed termination.

[0136] Subsequently, add the water 225 section at once, the 200 sections of this mixture were made to carry out phase inversion emulsification, adding and agitating the methyl-ethyl-ketone 50 section and the 1 convention aqueous ammonia 3.5 section, and the blue resin particle was formed in them. Since distributed stability was increased with the water 150 section as a dilution water, the 1 convention aqueous ammonia 4 section was added.

[0137] Subsequently, vacuum distillation removed the organic solvent and aqueous dispersion liquid were obtained. 1 convention hydrochloric-acid aqueous solution was added to this, PH was set to 2.5, the water slurry was processed with the centrifugal separator, fines were removed, subsequently to a filter (product made from Chisso Filter) the water slurry was passed, and the big and rough particle was removed. Stoving of the wet cake obtained by filtering and rinsing was carried out agitating under reduced pressure, and the powder of a blue resin particle (6% of pigment content) was obtained.

[0138] Volume mean particle diameter was 4.8 micrometers, and 50% volume particle size / 50% number particle size of this blue resin particle was the good particle size distributions [ square root / of 1.11 or 84% volume particle size / 16% volume particle size ] 1.19. When average circularity carried out TEM observation of this particle cross section in the globular form of 0.988, the endocyst of the phthalocyanine pigment was carried out to the particle, and it was distributed to homogeneity.

[0139] In this fine-particles 100 section, the 0.5 sections of titanium oxide particle MT-150 and the 2.8 sections of the hydrophobic silica RY200 (product made from Japanese Aerosil) were \*\* (ed) outside, and the globular form fine-particles toner 4 was prepared in it.

[0140] (Example 1 of a comparison of toner manufacture) After adding the 52 sections of the sodium hydroxide aqueous solution of 1 convention, the 75 sections of isopropyl alcohol, and the 130 sections of deionized water and mixing well to the 566 sections of the mill base, the black resin particle fine particles make into the purpose be obtained by the same actuation as the example 1 of toner manufacture except the deionized water 50 section having been dropped and having carry out phase inversion emulsification, holding and stirring inside \*\* at 30 degrees C.

[0141] The volume mean particle diameter of these fine particles was 7.8 micrometers, and 50% volume particle size / 50% number particle size was the good particle size distributions [ square root / of 1.10 or 84% volume particle size / 16% volume particle size ] 1.20. When average circularity observed this particle cross section by TEM in the globular form of 0.989, the endocyst of the carbon black pigment was carried out to the particle, and it was distributed to homogeneity.

[0142] In this fine-particles 100 section, the 0.5 sections of titanium oxide particle MT-150 and the 1.0 sections of the hydrophobic silica SLM50650 were \*(ed) outside, and the globular form fine-particles toner 5 was prepared in it.

[0143] (Example 2 of a comparison of toner manufacture) After fully carrying out desolventization of the mill base made from the example 1 of toner manufacture under reduced pressure, it ground, and, subsequently classified using the dry classifier, and volume mean particle diameter obtained the black resin particle fine particles of the average circularity 0.947 in which number particle size has the particle size distribution [ square root / of volume particle size ] 1.27, 50% volume particle size / [ 7.3 micrometers and ] 50% 1.24 or 84% volume particle size / 16%. The 0.5 sections of titanium oxide particle MT-150 and the 1.2 sections of the hydrophobic silica SLM50650 were \*(ed) outside in this fine-particles 100 section, and the fine-particles toner 6 of an indeterminate form was prepared.

[0144] (Example 3 of a comparison of toner manufacture) Carry out melting kneading of the polyester resin 940 section and the phthalocyanine pigment "Ket Blue 123" 60 section which were used in the example 4 of toner manufacture. since — it ground, and, subsequently classified using the dry classifier, and volume mean particle diameter obtained the blue resin particle fine particles (6% of pigment content) of 5.3 micrometers and the average circularity 0.941 in which number particle size has the particle size distribution [ square root / of volume particle size ] 1.32, 50% volume particle size / 50% 1.34 or 84% volume particle size / 16%. In this fine-particles 100 section, the 0.5 sections of titanium oxide particle MT-150 and the 2.7 sections of the hydrophobic silica RY200 were \*(ed) outside, and the fine-particles toner 7 of an indeterminate form was prepared in it.

[0145] (The example and the example of a comparison of a development trial) The nonmagnetic 1 component developer trial of seven sorts of fine-particles toners which carried out in this way and were prepared was performed as follows. The toner cartridge of a commercial 1 component printer (OKI micro line 400) was filled up with the fine-particles toner made as an experiment, \*\*\*\*\* of a test pattern was performed, and the image quality was evaluated about the item of fogging, definition, gradation nature, and image concentration (image concentration was measured using the Macbeth concentration meter). In addition, after \*\*\*\*(ing) by said printer and performing a chisel, you made it established about a color toner using the fixing unit of a silicone oil spreading mold.

[0146] The toner coating weight on a developer support roll exfoliated the toner on a developer support roll covering the fixed side with adhesive tape, and was measured by measuring the weight.

[0147] Moreover, the consumption of the toner when printing 1000 images of a test pattern continuously was measured. These results were summarized to table-1.

[0148]

[A table 1]

	使用した トナー	トナー 付着量	トナー 消費量	カブリ	解像性	階調性	画像濃度
実施例 1	トナー 1	0. 3 3	1 0. 1	なし	+	+	1. 6 0
実施例 2	トナー 2	0. 2 0	7. 2	なし	++	++	1. 5 8
実施例 3	トナー 3	0. 3 4	1 0. 2	なし	+	+	1. 2 2
実施例 4	トナー 4	0. 3 8	1 1. 3	なし	+	+	1. 5 0
比較例 1	トナー 5	0. 5 8	1 8. 0	なし	標準	標準	1. 5 6
比較例 2	トナー 6	0. 6 5	2 3. 0	なし	標準	標準	1. 5 5
比較例 3	トナー 7	0. 4 8	1 7. 6	あり	+	+	1. 4 8

トナー付着量：mg/cm<sup>2</sup>

トナー消費量：印刷1000枚当たりの量（g）

解像性、階調性で、+は標準より優れる、++はさらに優れる、の意。

[0149]

[Effect of the Invention] while being able to boil image quality markedly and being able to improve by using the development method of nonmagnetic 1 component by this invention, the toner consumption per one sheet of printing paper can be reduced sharply. In this development method, although the globular form toner of the diameter of a granule is used, the engine performance is further demonstrated by altitude by specifying the particle size distribution of this toner, a presentation, the manufacture method, etc.

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[Translation done.]



(5)In(Cl)	G03G	9/08	識別記号	PI
G03G	9/08	9/08	G03G	9/08
	9/08	15/08		504
	15/08	9/08		325
				331
				361

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審査請求 未請求 請求項の数8 OL (全13頁) 最終頁に続く

(54)【発明の名称】 粉体トナーによる画像形成方法

(57)【要約】  
 【課題】画像品質に優れ、かつページ当たりのトナー消費量の少ない非磁性一成分現像方法を提供する。  
 【解決手段】 少なくとも現像剤担持ロールと層形成部材とを有する非磁性一成分現像装置を用いて、感光体に現像剤を供給し、感光体上の静電潜像を顕在化する非磁性一成分現像方法に於いて、現像剤として体積平均粒径が2〜6μmである球形トナーを用い、現像剤担持ロール上のトナー付着量を0.1mg/cm<sup>2</sup>以上から0.45mg/cm<sup>2</sup>以下の範囲とすることによって解決を図った。さらに現像剤として使用する球形トナーの形状特性、使用する樹脂の種類と着色剤含有率、外添する無機酸化物微粒子の添加量を最適化して、本発明の効果および顕著に表現する条件を見出し、乳化法、重合法などの複合式でそのような球形トナーを製作するための最適な方法を見出した。

(2) 特開平11-218957  
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 るのに好適な、高品質な画像を形成しうる新規な非磁性一成分現像方法に関する。  
 【0002】  
 【従来の技術】 現状の電子写真方式の複写機やプリンタの画質は、平版印刷や銀塩写真などに比べると格段に劣り、画像形成装置とそれを使用される粉体トナーの両面から種々の改良がなされている。  
 【0003】 トナーの面からは、解像度などの画像品質を向上させる手段として、近年、ますます小粒径化が重要となり種々技術開発が行われている。  
 【0004】 しかしながら、現在市販されている静電荷像現像用の粉体トナーの大部分が体積平均粒径8〜13μm程度であり、最も小粒径なもので7μm程度である(粒径の測定はコールター・マルチサイザー(日科機器)による)。このように画質の高解像度化に極めて有用であるトナーの小粒径化に関しては、現在のところ7μm程度に止まっており、それよりも小粒径トナーの商業的な生産は行われていないし、そのようなトナーを使用する現像装置の開発もありなされていないのが実状である。  
 【0005】 そこで、トナーのさらなる小粒径化と優れた帯電性の付与、ならびにその現像方式の開発・出現が待たれている。  
 【0006】 粉体トナーは、その製法として、乾式法としては粉砕法であり、また湿式法としては重合法や、特開平5-66600号公報などに記載されているいわゆる転相乳化法とがある。粉砕法によるトナーでは、現状の粉砕機を用いた工業的生産では7μm程度の小粒径化の限界といわれている。勿論5μm程度の小粒径トナーも生産は可能であるが、コストアップになること、およびトナーの小粒径化に伴う摩擦帯電性や粉体流動性の悪化という問題があり実用的とはいえない。  
 【0007】 重合法や乳化法などの湿式法では、粉体トナーの小粒径化は基本的には困難性はないといわれている。しかしながら、従来の湿式法トナーでは、上記のような通常の平均粒径(7〜13μm程度)を持った粉砕トナーの置き換えを主たる開発あるいは生産目標にしており、平均粒径が6μm程度以下の小粒径である粉体トナーについては、現在までのところ断片的にしか知られておらず、実用的な処方分は分かっていない。  
 【0008】 一方、画像形成装置についても、画像品質向上のためトナーの小粒径化に対応した様々な研究がなされているが、上記したように、十分な小粒径を持つトナーが安定的に生産出来ないため、画像形成装置の側でもそのような小粒径のトナーに対応した画像形成方法も十分に開発することが出来なかった。このため現在のところ、高解像度の画像形成を可能にする、平均粒径が6μm程度以下の小粒径トナーに対応した、画像形成方法はいまだ十分確立していない。  
 【0009】

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 【特許請求の範囲】  
 【請求項1】 少なくとも現像剤担持ロールと層形成部材とを有する非磁性一成分現像装置を用いて、感光体に現像剤を供給し、感光体上の静電潜像を顕在化する非磁性一成分現像方法に於いて、現像剤として体積平均粒径が2〜6μmである球形トナーを用い、現像剤担持ロール上のトナー付着量が0.1mg/cm<sup>2</sup>以上から0.45mg/cm<sup>2</sup>以下の範囲であることを特徴とする非磁性一成分現像方法。  
 【請求項2】 現像剤として、結着用樹脂がステレン(メタ)アクリル樹脂で、着色剤がカーボンブラックで、該カーボンブラックの含有率が8重量%以上である球形トナーを用いる請求項1記載の非磁性一成分現像方法。  
 【請求項3】 現像剤として、結着用樹脂がポリエステル樹脂で、着色剤が有機顔料で、該有機顔料の含有率が3重量%以上である球形トナーを用いる請求項1記載の非磁性一成分現像方法。  
 【請求項4】 現像剤として、着色剤が結着用樹脂に内包された、平均円形度(粒子投影面積と同じ面積の円の周長)/粒子投影像の周長で定義される円形度の平均値が0.97以上の球形トナーを用いる請求項1、2又は3記載の非磁性一成分現像方法。  
 【請求項5】 現像剤として用いる球形トナーの粒度分布が、50%体積径/50%個数径が1.25以下で、かつ84%体積径/16%体積径の平方根が1.25以下である請求項1、2、3又は4記載の画像形成方法。  
 【請求項6】 現像剤として用いる球形トナー粒子に、無機酸化物微粒子が次式で示される量だけ外添されている請求項1、2、3、4又は5記載の非磁性一成分現像方法。  
 【式1】  
 3.5714X<sup>-0.9942</sup> ≤ Y ≤ 31.399X<sup>-0.9477</sup>  
 (ここでXはトナー粒子の体積平均粒径(μm)、Yはトナー粒子に対する外添量(重量%)。)  
 【請求項7】 トナー粒子が、着色剤と非水溶性の結着用樹脂を必須成分とする有機溶媒溶液と、水性媒体とを混合し、乳化させて球形着色微粒子を形成後、液媒体中に分散している微粒子を乾燥粉体として取り出す方法で得られたものである請求項4、5又は6記載の非磁性一成分現像方法。  
 【請求項8】 トナー粒子が、着色剤を分散させた重合性モノマーを、液媒体中で重合させて球形着色微粒子を形成後、液媒体中に分散している微粒子を乾燥粉体として取り出す方法で得られたものである請求項4、5又は6記載の非磁性一成分現像方法。  
 【発明の詳細な説明】  
 【0001】  
 【発明の属する技術分野】 本発明は、電子写真方式のプリンターや複写機などに於ける、静電荷像現像に使用する

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 【0009】



【0016】

【式1】

3.  $5.714 \times 10^{-0.9942} \leq Y \leq 31.399 \times 10^{-0.9477}$ 

(ここでXは粒子(C)の体積平均粒径( $\mu\text{m}$ )、Yは粒子(C)に対する外添量(重量%)。)

【0017】これは、上記条件を満たしたトナーを用いることによって、トナーの重要な基本的特性である帯電性や流動性を著しく改良できるからである。

【0018】さらにまた発明者らは、着色剤と非水溶性の結着用樹脂を必須成分とする有機溶媒溶液と、水性媒体とを混合し、乳化させて球形着色微粒子を形成後、液体媒体中に分散している微粒子を乾燥粉体として取り出し、方法で得られたものである粉体トナー、もしくは、着色剤を分散させた重合性モノマーを、液媒体中で重合させて球形着色微粒子を形成後、液媒体中に分散している微粒子を乾燥粉体として取り出す方法で得られたものである粉体トナーを用いることによって、上記本発明の非磁性・成分現像法に適合したトナー粒子を容易に得ることが出来ることを見出した。

【0019】以下に本発明に至った経緯と発明の詳細について述べる。

【0020】本発明者らは、解像性、階調性、カブリ、画像濃度などの画像品質を向上させるためには、トナーの小粒径もさることながら、画像形成装置にかかわる画像形成方法の最も基本的なところにおいて、その条件を高画質化に適した条件に設定することに着目して鋭意検討した結果、現在実用化されている非磁性・成分現像装置に於ける現像剤保持ロール上のトナー付着量、0.5～0.7mg/cm<sup>2</sup>程度に対し、0.1～0.45mg/cm<sup>2</sup>に、さらに望ましくは0.2～0.4mg/cm<sup>2</sup>に設定することにより、画像品質を著しく向上させることができることを見出した。

【0021】現像剤保持ロール上のトナー付着量が多いと、感光体を介して、被印体上に過剰のトナーが転写される結果、印刷画像の解像性や階調性の低下を引き起こす。また現像剤保持ロール上のトナー付着量が少なくなると印刷画像の濃度が不十分となり実用性に欠ける。【0022】画像品質を格段に向上させるには、被印体上のトナー層の厚みを適切な範囲に制御することが必要で、そのためには現像剤保持ロール上のトナー付着量を最適な範囲に設定することが不可欠である。本発明者らは、このような画像品質の向上に最適な特性を持つ粉体トナーを見いだすとともに、そのようなトナーを安定製造できる手法の開発に成功し、さらにそのトナーを用いて画像の品質を格段に向上させることが可能な上記最適付着量からなる画像形成方法を見出した。

【0023】本発明にかかる、現像剤保持ロール上のトナー付着量を実現するためには、トナーの粒径を小さくするとともに、必要な粉末流動性を確保するためにトナ一形状は球形が好適である。

【0024】本発明者らは、現像剤保持ロール上のトナー付着量を前記の最適値に調整するためのトナーの粒径は、体積平均粒径にして2～6 $\mu\text{m}$ 、さらに望ましくは3～5.5 $\mu\text{m}$ であることを見出した。

【0025】現状の粉体トナーによって印刷された画像のトナー層の厚みは、平版印刷インキなどによって印刷された高品質な画像のインキ層の厚みに比べて著常に厚くなっているが、画像品質向上のためには、印刷された画像のトナー層の厚みを現状よりも薄くすることが重要である。トナーを小粒径化し、現像剤保持ロール上のトナー付着量を減少させ、画像形成に關与するトナー量が減少するため、画像の濃度低下が起こりやすい。そこでトナーの着色剤含有率を増加させて、必要な画像濃度を確保する必要がある。

【0026】従って、本発明が対象とする2～6 $\mu\text{m}$ という小粒径トナーで十分な印刷画像濃度を得るには、トナーの顔料濃度をある程度以上に設定することが不可欠であり、市販の普通サイズ(7 $\mu\text{m}$ ～13 $\mu\text{m}$ 程度)のトナーよりも高い着色剤濃度にする必要がある場合がある。

【0027】本発明の2～6 $\mu\text{m}$ の粉体トナーでは、着色剤にカーボンブラック顔料を用いた黒色トナーにおいては、結着用樹脂と着色剤の合計重量に対する重量%以上、更に望ましくは9重量%以上含有させる必要がある。また、着色剤に有機顔料を用いたカラートナーに於いては、結着用樹脂と着色剤の合計重量に対する重量%以上、更に望ましくは4重量%以上含有させる必要がある。

【0028】黒色用トナーに関しては、スチレンアクリル樹脂を結着用樹脂に用いることで着色の制御が容易になり本発明に好適である。またカラートナーに関しては、ポリエステル樹脂を結着用樹脂に用いることでより優れた彩色性や光沢が得られるので本発明に好適である。

【0029】さらにまた、トナー粒子の平均円形度(粒子投影面積と同じ面積の円の周長)/粒子投影像の周長で定義される円形度の平均値が0.97以上、より好ましくは0.98以上の粒子であることを特徴とする粉体トナーを用いることによって、上記現像剤保持ロール上のトナー付着量を容易に達成できる。これは、このような真球度の高い球形がしかも小粒径のトナーを用いることによって、現像剤保持ロール上に均一に薄いつナー層が形成されやすからである。

【0030】粉体法による粉体トナーを小粒径化してゆく場合においては、平均粒径が6 $\mu\text{m}$ 程度から、急激に粉砕エネルギーが増大するだけでなく、得られるトナー粒子の形状が不定形であるため、得られるトナーの帯電性や粉末流動性が悪化する。これが6 $\mu\text{m}$ 程度以下の小粒径トナーを実用化する上での大きな問題点である。

【0031】しかしながら、トナーの小粒径化による粉末流動性の低下は、トナーの粒子形状を球形化することにより大きく改善でき、本発明が対象とする2～6 $\mu\text{m}$ の小粒径トナーでは平均円形度0.97以上が必要である。この平均円形度は、トナー粒子のSEM(走査型電子顕微鏡)写真を撮影し、それを測定し計算することなどによって求められるが、真面目医用電子(株)製フロン式粒子像分析装置FPIP-1000を使用すると容易に測定できる。

【0032】さらに一方、小粒径化による帯電性の悪化に関しては、含有する着色剤やその他の添加物(通常ワックスや帯電制御剤など)の一部がトナー粒子表面に露出することによって主たる原因があるものと本発明者らは推察している。即ち、着色剤等の含有率(重量%)が同じであっても、小粒径化によりトナー粒子の表面積が増大し、トナー粒子表面に露出する着色剤等の比率が増大し、その結果、トナー粒子表面の組成が大きく変化する。トナー粒子の帯電帯電性能が大きく変わり、制御が難しくなるわけである。

【0033】トナーを小粒径化しても帯電帯電性能を良好に保持するには、着色剤等がトナー粒子表面に露出しないようにすること、即ち着色剤等がトナー粒子に内包されるトナー構造にすることが有効である。

【0034】トナー粒子表面に着色剤や帯電制御剤(CA)、ワックス等が露出していないことは、例えば粒子の断面をTEM(透過型電子顕微鏡)で観察することにより容易に判定できる。より具体的には、トナー粒子を樹脂包埋してミクロトームで切断した断面を、必要ならば酸化アルミニウム等で染色し、TEMで観察すると、着色剤等が粒子に内包されているかどうかは明瞭に分かる。

【0035】上記のような着色剤等がトナー粒子に内包された2～6 $\mu\text{m}$ の小粒径球形トナーは、理論的には、粉砕法で作った不定形の粒子を樹脂で表面処理するなどして球形化することによっても得ることが可能であるが、製造の容易さやコスト等から、重合法や乳合法などのような複式法によって作るのが実際的であり好適である。とりわけ、乳合法は、結着用樹脂の種類を幅広く変えても粒度分布の良好な球形着色粒子が形成でき、また原料の純度のアップが容易であることなどから、本発明の粉体トナーの製法として特に好適である。

【0036】またこのような方法を用いたほうが、以下に述べるようなトナーの粒径分布もシャープなものである。【0037】トナー粒子の粒度分布も帯電性能に影響を与えるが、知見として、特に本発明が対象とする小粒径トナーでは、現在商品化されている7～13 $\mu\text{m}$ 程度のトナーよりもよりシャープな粒度分布が要求される。即ち、本発明の対象である体積平均粒径が2～6 $\mu\text{m}$ の粉体トナーに於いては、コールタマナチサイザーによる測

方法では、現像剤保持ローラ上のトナー付着量を0.1 mg/cm<sup>2</sup>以上で0.45 mg/cm<sup>2</sup>以下の範囲に設定することを特徴としており、これによって著しい画像の品質向上が達成できるが、トナー付着量をこの範囲に設定し、なおかつよりよい画像品質を持つようにする場合には、前記したように使用するトナーについても、組成や製法等についてより望ましい条件を設定する必要がある。

【0048】以下に、これら本発明の画像形成方法で用いるトナーの好適な組成や製法について、その詳細を述べる。

【0049】本発明の粉体トナーに使用される着色剤としては、特に制限はなく、従来、電子写真用トナー等で使用されてきた着色剤を用いることができ、顔料が好ましく、以下のようないものが例示できる。

【0050】黒色顔料としては、例えば、カーボンブラック、シアニブラック、アニリンブラック、フェライト、マグネタイト等が挙げられる。又は、以下の有彩色顔料を黒色となる様に調製したものを使用することが出来るが、カーボンブラックがより好適である。

【0051】黄色顔料としては、例えば、黄鉛、亜鉛黄、カドミウムイエロー、黄色酸化鉄、黄土、チタン黄、ナフトールイエロー-S、ハンザイエロー10G、ハンザイエロー5G、ハンザイエロー-G、ハンザイエローGR、ハンザイエロー-A、ハンザイエロー-RN、ハンザイエロー-R、ビグメントイエロー-L、ベンジンイエロー、ベンジンイエロー-G、ベンジンイエロー-GR、ベンジンイエロー-NCG、バルカンファーストイエロー5G、バルカンファーストイエロー-R、キノリイエローレーキ、アンストラヴァンイエロー6GL、バーメントイエロー-FGL、バーメントイエロー-H10G、その他イソインドリノンイエロー、クロモフタルイエロー、ノボバーメイエロー-H2G、縮合アゾイエロー、ニッケルアゾイエロー、銅アゾメチンイエロー等が挙げられる。

【0052】赤色顔料としては、例えば、赤色黄鉛、セリブデンオレンジ、バーメントオレンジGTR、ピラソルオレンジ、バルカンオレンジ、インダストリアル

リアントオレンジRK、インダストリアルリアントオレンジGK、ベンジンオレンジG、バーメントレッド4R、バーメントレッドBL、バーメントレッド5RK、リゾールレッド、ピラソルレッド、ウォッチングレッド、レーキレッドC、レーキレッドD、ブリリアントカーミン6B、ブリリアントカーミン3B、ロダミンレーキB、アリザリンレーキ、バーメントカーミンFBB、ペリゾレンジ、イソインドリノンオレンジ、アンスアンソロンオレンジ、ピラソロンオレンジ、キナクリドンレッド、キナクリドンマゼンタ、キナクリドンスカーレット、ペリレンレッド等が挙げられ

る。

【0053】青色顔料としては、例えば、コバルトブルー、セリブデンブルー、アルカリブルーレーキ、ヒューコックブルーレーキ、フアトーンブルー6G、ビクトリアブルーレーキ、無金属フタロシアニンブルー、銅フタロシアニンブルー、ファーストスカイブルー、インダストリアルRS、インダストリアルブルーBC、インジコ等が挙げられる。

【0054】本発明に使用するトナー粒子の乳化法による作り方は次のようである。着色剤と非水溶性の結着剤を混合し、乳化する溶剤系樹脂を形成後、有機溶媒を除去し、水性媒体中に分散している顔料粒子を乾燥粉体として取り出し、必要であれば分級を行って粒度分布を整え、トナー粒子を作る。

【0055】結着剤樹脂の溶解および着色剤等の分散のために用いられる前記有機溶媒としては、例えばベンゼン、ヘキサン、ヘプタン、ペンゼン、トルエン、キシレン、シクロヘキサン、石油エーテルなどの炭化水素類；強化メチレン、クロロホルム、ジクロロエタン、ジクロロエチレン、トリクロロエタン、トリクロロエチレン、四塩化炭素などのハロゲン化炭化水素類；メタノール、エタノール、イソプロピルアルコール、n-プロピルアルコール、ブタノールなどのアルコール類；アセトン、メチルエチルケトン、メチルイソブチルケトンなどのケトン類；酢酸エチル、酢酸ブチルなどのエステル類；などが挙げられ、これらの二種以上を混合して用いてもよい。

【0056】前記結着剤樹脂としては、上記有機溶媒に可溶であればよく、特に限定はないが、それ自体では水性媒体に分散せず乳化剤または分散安定剤を用いて初めて水性媒体に分散しうる非水溶性樹脂と、それ自体で水性媒体に分散しうる、「自己分散性」を有する非水溶性樹脂とがある。

【0057】この様なトナー用の非水溶性樹脂として、例えば、スチレン系樹脂、（メタ）アクリル系樹脂、ポリエステル系樹脂、ポリウレタン系樹脂あるいはエポキシ系樹脂などがある。中でも、スチレン系モノマーと（メタ）アクリル酸エステルを必須成分として混合され、いわゆるスチレン（メタ）アクリル樹脂が好適である。本発明において、（メタ）アクリルには、メタアクリルとアクリルを含む。

【0058】前記樹脂としては、充分な機械的強度を発現するに必要ないレベルの分子重、通常重量平均分子量として3000〜300000、かつ、DSC（示差走査熱量計）測定において、ガラス転移温度（T<sub>g</sub>）が50〜100℃であるものが好適である。

【0059】前記結着剤樹脂の内で、自己分散性樹脂とは、中和によりアニオン型となりうる官能基を含有した樹脂で、それら親水性となりうる官能基の一部または

全部が塩基で中和された、水性媒体の作用下で、乳化剤または分散安定剤を用いることなく安定した水分散体形成できる樹脂をいう。

【0060】中和により親水性基となりうる官能基としては、例えば、カルボキシル基、燐酸基、スルホン基などのいわゆる酸性基が挙げられる。これら官能基を含有する樹脂としては、スチレン系樹脂、（メタ）アクリル系樹脂、ポリエステル系樹脂、ポリウレタン系樹脂、エポキシ系樹脂などが挙げられる。この様な中でも、酸基を有するスチレン（メタ）アクリル樹脂が好適に用いられる。

【0061】本発明で用いるのに好適な、中和により自己分散性となりうるアニオン型スチレン（メタ）アクリル樹脂としては、スチレン系モノマーを必須成分として酸基を含有した（メタ）アクリル系重合性ビニル単量体と、この酸基を含有した重合性ビニル単量体以外の（メタ）アクリル酸エステルに代表される重合性ビニル単量体を、ラジカル開始剤存在下でラジカル重合させて得られるものが使用できる。それを得るための重合反応は、溶液重合でも、懸濁、乳化重合でも適宜利用できる。

【0062】こうした酸基含有（メタ）アクリル系重合性単量体類としては、例えば、アクリル酸、メタクリル酸、クロトン酸、イタコン酸、マレイン酸、フマル酸、イタコン酸モノブチル、マレイン酸モノブチルなどが挙げられる。

【0063】酸基含有重合性単量体類以外の重合性単量体としては、例えば、スチレン系モノマー（芳香族ビニルモノマー）類として、スチレン、ビニルトルエン、2-メチルスチレン、1-ブチルスチレンもしくはクロルスチレンがある。

【0064】アクリル酸エステル類としては、例えばアクリル酸メチル、アクリル酸エチル、アクリル酸イソプロピル、アクリル酸n-ブチル、アクリル酸n-ペンチル、アクリル酸n-ヘキシル、アクリル酸2-エチルヘキシル、アクリル酸n-オクチル、アクリル酸デシルもしくはアクリル酸ドデシル、アクリル酸2-クロロエチル、アクリル酸フェニル、アルファクロロアクリル酸メチルなどが挙げられる。

【0065】メタクリル酸エステルとしては、例えばメタクリル酸メチル、メタクリル酸プロピル、メタクリル酸n-ブチル、メタクリル酸イソブチル、メタクリル酸n-ペンチル、メタクリル酸n-ヘキシル、メタクリル酸2-エチルヘキシル、メタクリル酸n-オクチル、メタクリル酸デシル、メタクリル酸ドデシル、メタクリル酸2-クロロエチル、メタクリル酸フェニル、アルファクロロメタクリル酸メチルなどが挙げられる。

【0066】また、アクリロニトリル、メタアクリロニトリル、アクリルアミド等のアクリル酸もしくはメタク





アクリル酸ブチル  
アクリル酸  
「パーブチルO」

[0125] 滴下終了後、3時間毎に3回「パーブチルO」の2部を添加し、さらに4時間反応を継続してから終了した。その後、脱溶剤を行い、固形樹脂(R-2)を得た。この樹脂のガラス転移温度は61℃、重量平均分子量は124000、酸価は70であった。

[0126] (トナー製造の実施例1) R-202000部と、カーボンブラック(キャボット社製E1FTE X8)の5000部とを、ニーダーを使用して1時間の間混練せしめた。このマスターバッチの樹脂固形分(原料)割合は、80/20になる。このマスターバッチ750部と、R-2の固形樹脂450部と、R-1の固形樹脂300部とをメチルエチルケトン(1000部)に溶解し、次に得られたカーボン分散樹脂溶液に、ワックス分散体「H808」(東京油脂社製のエマルジョン型ワックス、フイジシャートロブジュワックス、粒子径0.5μm、固形分含有量30%)の150部を添加し、「アイガー・モーター・ミル M-250」を使って10分間のめいど混合・分散させた。ついで、メチルエチルケトンで不揮発分濃度を5.3%に調整し、ミルベースを作製した。

[0127] 次いで、このミルベースの560部に対して、1規定の水酸化ナトリウム水溶液の4.8部およびイソプロピルアルコールの5.8部及び、脱イオン水の150部を加え、良く混合した後、内温を30℃に保持し、攪拌しながら脱イオン水43部を滴下し転相化させ樹脂微粒子を形成させた。さらに、30分後に脱イオン水の5000部を添加した。

[0128] 次に、減圧蒸留によって有機溶剤を除去し、水媒体より樹脂微粒子を濾別した。このうち、当粒子を水中に再分散させた。続いてこの分散液を、0.1N塩酸水溶液にてpH2に調整し、30分間攪拌してから、この水スラリーを遠心分離機で処理して微粉を除去し、次いで水スラリーをフィルタ(チソソフィルタ(株)製)に通通させて粗大粒子を除去した。水スラリーを濾別した後、さらに水中に再分散洗浄する操作をした後、樹脂微粒子を水媒体より分離させウェットケーキを得、これを乾燥乾燥させ、青色樹脂微粒子の粉末とした。

[0129] 得られた青色樹脂微粒子の体積平均粒子径は、コールター・マルチサイザー2を用いた測定により、5.0μmで、50%体積径/50%体積径/50%体積径/1.10、84%体積径/16%体積径の平方根が1.21という良好な粒度分布であった。東亜電用電子(株)製フロー式粒子像分析装置FPIP-1000で測定すると平均円形度が0.989の球形であった。この粒子を樹脂包埋ミクロトームで切削した断面をTEM(透過型電子顕微鏡)で観察したところ、カーボンブラック原料は粒子に内包されて均一に分散していた。

を添加した。

[0137] 次いで、減圧蒸留により有機溶剤を除去し、水媒体分散液を得た。これに1規定塩酸水溶液を加えてpHを2.5とし、水スラリーを遠心分離機で処理して微粉を除去し、ついで水スラリーをフィルタ(チソソフィルタ(株)製)に通通させて粗大粒子を除去した。濾過・水洗して得られたウェットケーキを、減圧下に攪拌しながら加熱乾燥して、青色樹脂微粒子(原料含有率6%)の粉末を得た。

[0138] この青色樹脂微粒子は体積平均粒子径が4.8μmで、50%体積径/50%体積径/50%体積径/1.11、84%体積径/16%体積径の平方根が1.19という良好な粒度分布であった。平均円形度が0.988の球形で、この粒子断面をTEM観察したところ、フクロンアミン原料は粒子に内包されて均一に分散していた。

[0139] この粉体100部に、酸化チタン微粒子MT-150の0.5部および疎水性シリカRY200(日本アエロゾル社製)の2.8部を外添し球形の粉体トナー4を調製した。

[0140] (トナー製造の実施例1) ミルベースの560部に対して、1規定の水酸化ナトリウム水溶液の5.2部およびイソプロピルアルコールの7.5部及び、脱イオン水の130部を加え、良く混合した後、内温を30℃に保持し、攪拌しながら脱イオン水50部を滴下し転相化させた。これはトナー製造の実施例1と同様の操作により、目的とする青色樹脂微粒子粉体を得た。

[0141] この粉体の体積平均粒子径は7.8μmで、50%体積径/50%体積径/50%体積径/1.10、84%体積径/16%体積径の平方根が1.20という良好な粒度分布であった。平均円形度が0.989の球形で、この粒子断面をTEMで観察したところ、カーボンブラック原料は粒子に内包されて均一に分散していた。

[0142] この粉体100部に、酸化チタン微粒子MT-150の0.5部および疎水性シリカSLM50650の1.0部を外添し球形の粉体トナー5を調製した。

[0143] (トナー製造の実施例2) トナー製造の実

施例1で作ったミルベースを減圧下で十分に脱溶剤してから、粉砕し、次いで乾式分級機を用いて分級し、体積平均粒子径が7.3μm、50%体積径/50%体積径/1.24、84%体積径/16%体積径の平方根が1.27という粒度分布を有する、平均円形度0.947の青色樹脂微粒子粉体を得た。この粉体100部に酸化チタン微粒子MT-150の0.5部および疎水性シリカSLM50650の1.2部を外添して不定形の粉体トナー6を調製した。

[0144] (トナー製造の実施例3) トナー製造の実施例4で使ったゲルエスチル樹脂940部とフクロンアミン原料「Ket Blue 123」60部を溶解し、体積平均粒子径が5.3μm、50%体積径/50%体積径/1.34、84%体積径/16%体積径の平方根が1.32という粒度分布を有する平均円形度0.941の青色樹脂微粒子粉体(原料含有率6%)を得た。この粉体100部に、酸化チタン微粒子MT-150の0.5部および疎水性シリカRY200の2.7部を外添して不定形の粉体トナー7を調製した。

[0145] (現像試薬の実施例および比較例) このようにして調製した7種の粉体トナーの非磁性成分分現像試験は次のように行った。市販の成分分プリンター(OKIマイクロライオン400)のトナーカートリッジに、試作した粉体トナーを充填し、テストパターン(の面出しを行い、その画像品質をカブリ、解像性、階調性、画像濃度の項目について評価した(画像濃度はマクベス濃度計を使用して測定した)。尚、カラートナーについては、前記プリンターで画出しのみを行って、シリコンオイル塗布型の定着ユニットを用いて定着させた。

[0146] 現像剤保持ロール上のトナー付着量は、現像剤保持ロール上のトナーを接着テープにて一断面にわたって剥離し、その重量を測ることによって測定した。

[0147] また、テストパターン(の画像を1000枚通照して印刷したときのトナーの消費量を測定した。これらの結果を表1にまとめた。

[0148]  
[表1]

	使用したトナー トナー	トナー 付着量	トナー 消費量	カブリ	解像性	階調性	画像濃度
実施例1	トナー1	0.93	10.1	なし	+	+	1.60
実施例2	トナー2	0.20	7.2	なし	++	++	1.58
実施例3	トナー3	0.34	10.2	なし	+	+	1.22
実施例4	トナー4	0.38	11.3	なし	+	+	1.50
比較例1	トナー5	0.58	18.0	なし	標準	標準	1.56
比較例2	トナー6	0.65	23.0	なし	標準	標準	1.55
比較例3	トナー7	0.48	17.6	あり	+	+	1.48

トナー付着量:mg/cm<sup>2</sup>

トナー消費量:印刷100枚当たりの量(g)

解像性、階調性で、+は標準より優れる、++はさらに優れる、の意。

[0149]

【発明の効果】本発明による非磁性一成分の現像方法を  
用いることにより、画像品質を格段に向上することがで  
きるとともに、印刷紙1枚当たりのトナー消費量を大幅

に低減することができる。本現像方法においては、小粒  
径の球形トナーを用いるが、該トナーの粒度分布、組  
成、製造方法等を特定化することにより、さらにその性  
能を高度に発揮させられる。

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